

Phosphate-Containing Flame-Retardant Polymers with Good Compatibility to Polypropylene. II. Effect of the Flame-Retardant Polymers on Polypropylene

WEN-YEN CHIANG,¹ HOWARD C.-H. HU²

¹ Department of Chemical Engineering, Tatung University, 40, Chungshan North Road, 3rd Sec., Taipei 104, Taiwan, People's Republic of China

² Polymer Technology Division, Union Chemical Laboratories, Industrial Technology Research Institute, 321, Kuang-Fu Road, 2nd Sec., Hsinchu 300, Taiwan, People's Republic of China

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ABSTRACT: Two kinds of flame-retardant polymers prepared from the phosphorylation of poly(vinyl acetate) were employed to reduce the flammability of polypropylene (PP). The two flame-retardant polymers had very different effects because of the differences in their chemical structure. Effects on flame retardancy, thermal properties, mechanical properties, and phase morphology were investigated. Under a certain molecular design, the flame-retardant polymers were able to offer good flame retardancy, good mechanical properties, and good PP matrix compatibility. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2399–2403, 2001

Key words: flame-retardant polypropylene; compatible; intumescence; phosphate

INTRODUCTION

Based on the demands of low smoke, corrodibility, and toxicity for flame-retardant polymeric materials, intumescent flame retardants were developed as a surrogate for traditional halogen-containing flame retardants. An early successful example of this is the ammonium polyphosphate (APP)/pentaerythritol/melamine (MN) three-component flame-retardant additive system. In this system, APP acts as a dehydrating catalyst,^{1,2} the pentaerythritol acts as a char source, and the MN is employed as a foaming agent, which expands the thickness and volume of the char layer and increases the thermal-shield effect of the char layer.^{3–5}

A polyol is especially necessary for the polyolefin matrix in intumescent systems because polyolefins do not have any functional group for dehydration and char forming. However, for some matrices that contain alcohol or amide groups, the polyol is not so important. Although polyvinyl alcohol (PVA) is also a polyol, it is seldom employed in intumescent systems because of its high crystallinity. A common solution for this is to reduce its crystallinity by grafting phosphorylation.^{8,9} However, the dehydration tendency of phosphorylated PVA is strong, so the thermal stability is not high enough for the application of melt compounding.

The drawbacks of the previously mentioned intumescent flame-retardant system include bad matrix compatibility, poor mechanical properties, moisture sensitivity, and migration. In this research, flame-retardant polymers prepared from the partial phosphorylation of poly(vinyl acetate) (PVAc) were able to conquer the problems men-

Correspondence to: W.-Y. Chiang (chiang@che.ttu.edu.tw).
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tioned previously. Phenyl groups and stearyl groups were added into the polymer-type flame retardant for the purposes of thermal stability and polypropylene (PP) matrix compatibility. Another flame retardant without those groups was also prepared and employed in the preparation of flame-retardant PP (FRPP) as an experimental reference.

EXPERIMENTAL

The PP used in this study had a melt flow index of 4 g/10 min and was purchased from Taiwan Propylene Co. The phosphate-containing flame-retardant polymers with various phosphate contents were prepared in our laboratory previously. MN (Hayashi Pure Chemical Industry Ltd.) was employed as a foaming agent to assist the intumescent effect of the flame-retardant polymers.

The compounding process for preparing the FRPP blends was carried out in a Brabender PLE-330 plasticorder at 190°C for 8 min with a rolling rate of 70 rpm. The blends contained PP (70 wt %, 35 g), phosphate-containing polymers (28.7 wt %, 14.35 g), and MN (1.3 wt %, 0.65 g). The codes of the phosphate-containing polymers with different substituents and substitution ratios are shown in Table I of part I of this series.

The test specimen was prepared by melt compression molding at 190°C. The tensile-test specimen, 1 mm thick, was molded according to ASTM standard D638 type IV. The Izod notched impact strength of the sample specimen, 3 mm thick, was measured according to the ASTM standard D256 with an impact energy of 30 kg/cm. The flame retardance of the sample was evaluated by a limiting oxygen index (LOI) test with a SUGA ONI model ON-1 meter. This measurement was carried out according to ASTM standard D2863-70.

RESULTS AND DISCUSSION

A successful design for flame-retardant additives for melt compounding needs to have two basic properties: a sufficient thermal stability during compounding and a good matrix compatibility. Hence, these two conditions were used to evaluate the phosphate-containing polymers for the application of FRPP in this study. We reported in the first part of this series that two phosphate-containing polymers prepared with two different phosphate substituents, SPPC and DECPa, were coded as S products and D products, respectively.

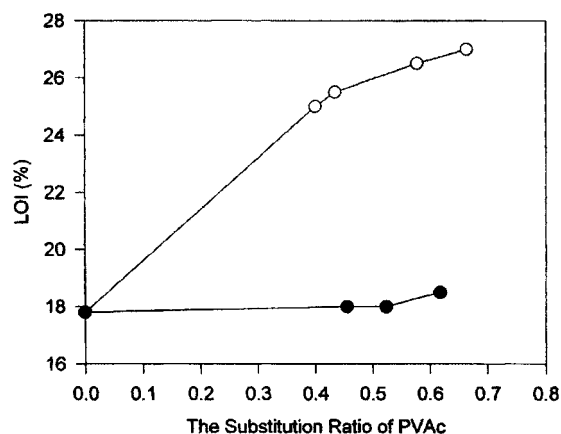


Figure 1 Flame-retardance performance in the LOI of the FRPP with different flame retardants: product S (○), product D (●), and different substitution ratios.

Figure 1 shows that the flame-retardant effect of the S products was good; however, that of the D products was very poor. It was reported in part I that the dehydrating tendency of the D products was stronger than that of the S products. A stronger dehydrating tendency represents a poorer thermal stability in this case. The FRPP employing the D products as flame retardants started to dehydrate during the melt blending process and produced a lot of visible char particles. The char particles in the materials decreased all the mechanical properties investigated in this study. Furthermore, the char did not cause any flame-retardant effect in the later fire test, so it did not increase the LOI value of the materials. The enhancing effect of the flame-retardant S polymers on the materials was caused by their sufficient thermal stability in melt blending, so the dehydration reaction could be initiated in the fire test.

The matrix compatibility of the flame retardant, the second important property, is closely related to the mechanical properties of the materials. Figures 2 and 3 show that the tensile yield strength and the Young's modulus of materials decreased after the addition of flame-retardant polymers; however, the S products showed an increasing effect on impact strength and elongation to the materials. The ester and phosphate ester structures in the S products decreased the degree of crystallinity of PP and offered a good impact-energy-absorbing ability.

The thermogravimetric analysis (TGA) diagram in Figure 4 shows the flame-retardant effect of the S products on PP. The S products caused the initiation of weight loss to occur in advance because the dehydration reaction was started.

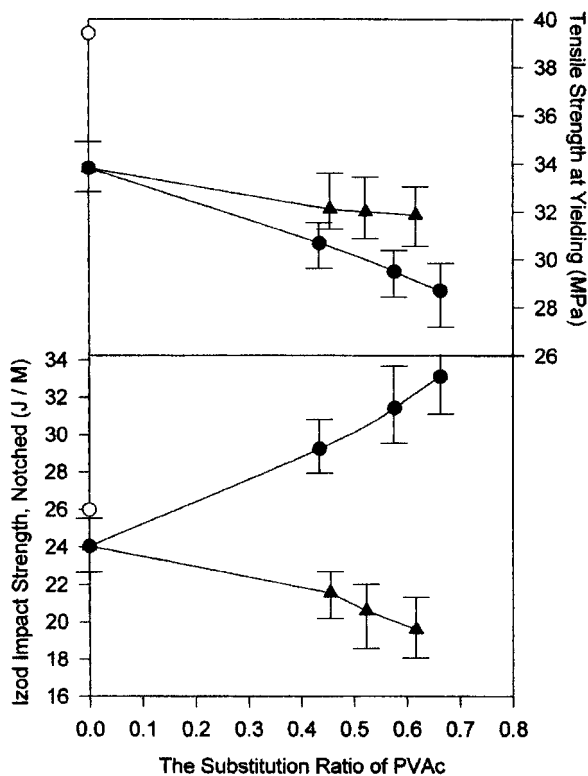


Figure 2 Tensile yield strength and Izod impact strength of PP (○) and the FRPP with different flame retardants: product S (●), product D (▲), and different substitution ratios.

The reaction promoted the yield of intermediate char at 350–420°C, which was a good barrier to heat and mass transfer. It can be more clearly found in the derivative weight loss shown in Figure 5 that the degradation rate peaks moved to higher temperatures and that the maximum degradation rates also decreased. The burned char of the FRPP with S products was collected for a Fourier transform infrared (FTIR) analysis, and the result, in which the P—O—P (980 cm^{-1}) and P—O—C (1000 cm^{-1}) structures were found, is shown in Figure 6. In the TGA analysis, although the final char produced under 800°C did not increase too much, the flame-retardant effect is believed to be conferred more by the intermediate char than by the final char.

Evidence of the decrease of the degree of crystallinity of PP by flame-retardant polymers was found in a DSC analysis (Fig. 7). The glass-transition temperature (T_g) of PP is not obvious because it is a crystalline polymer. The T_g of the material appeared at about 36°C after the introduction of PVAc. The T_g shifted to lower temperatures when the phosphate substitution ratio of PVAc was increased. Besides the T_g , the T_m of the

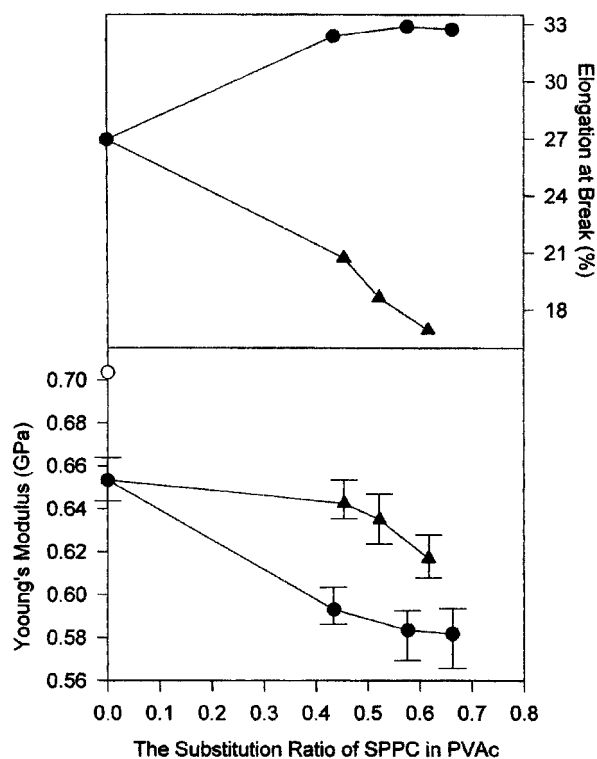


Figure 3 Elongation and Young's modulus of PP (○) and the FRPP with different flame retardants: product S (●), product D (▲), and different substitution ratios.

materials also shifted to lower temperatures. The decrease of T_g represents an increase of intramolecular mobility, which means some segments of the molecules more easily stretch, rotate, or vibrate. This intramolecular mobility increases the impact strength and elongation of the materials. The shifting of T_g and T_m also signifies that the

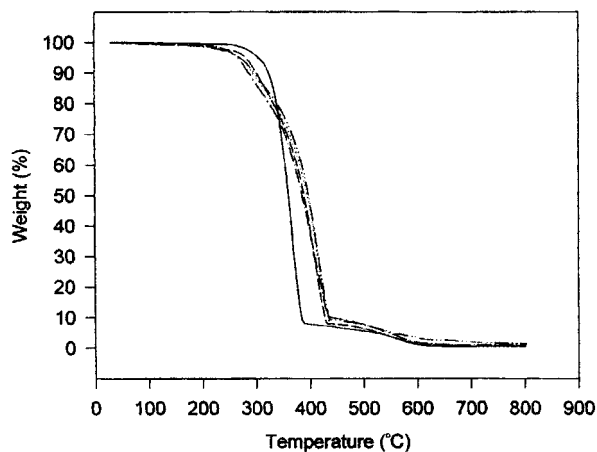


Figure 4 TGA diagram of the FRPP with PVAc (—) and products S04 (···), S05 (---), S06 (-·-), and S07 (-·-·).

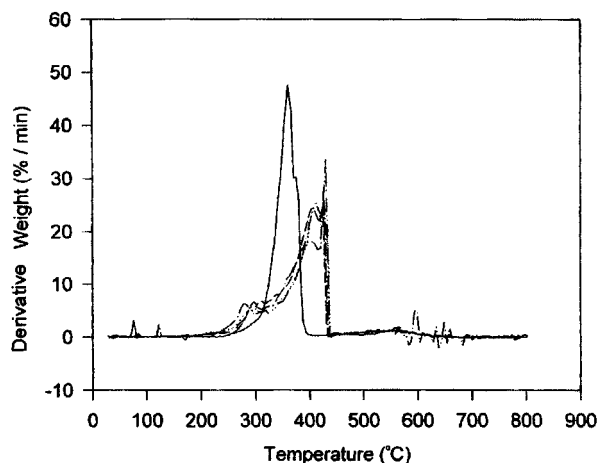


Figure 5 DTG diagram of the FRPP with PVAc (—) and products S04 (···), S05 (---), S06 (-·-), and S07 (-·-·-).

compatibility of the flame-retardant polymer and the PP matrix must be good.

Figure 8 shows scanning electron microscope photographs of the materials. Figures 8(a) and 8(b) show a PP continuous phase and a PVAc dispersed phase. The diameter of the dispersed phase ranged from about 40 to 100 μm . Some fine particles 10 μm in size found in Figure 8(b) are MN, the foaming agent. Figures 8(c), 8(d), and 8(e) show the fracture surface of FRPP with flame-retardant polymers S05, S06, and S07. As seen in a comparison of the two sets of photos, there are two major differences. One is the change of the dispersed phase. Comparing Figures 8(a)

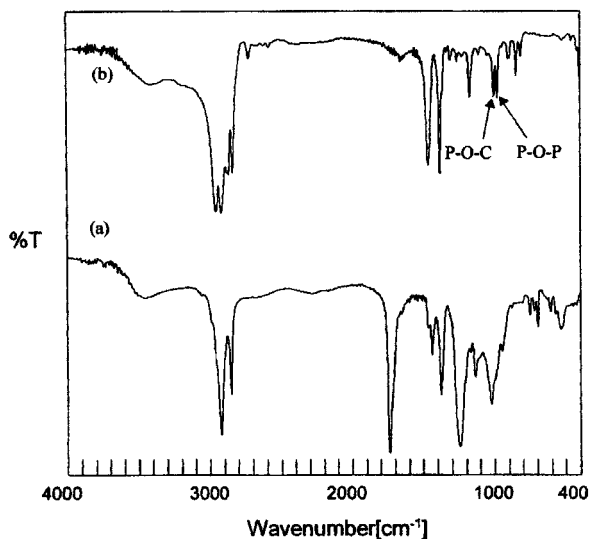


Figure 6 FTIR spectra of (a) product S05 and (b) burned char of the FRPP with S05 as a flame retardant.

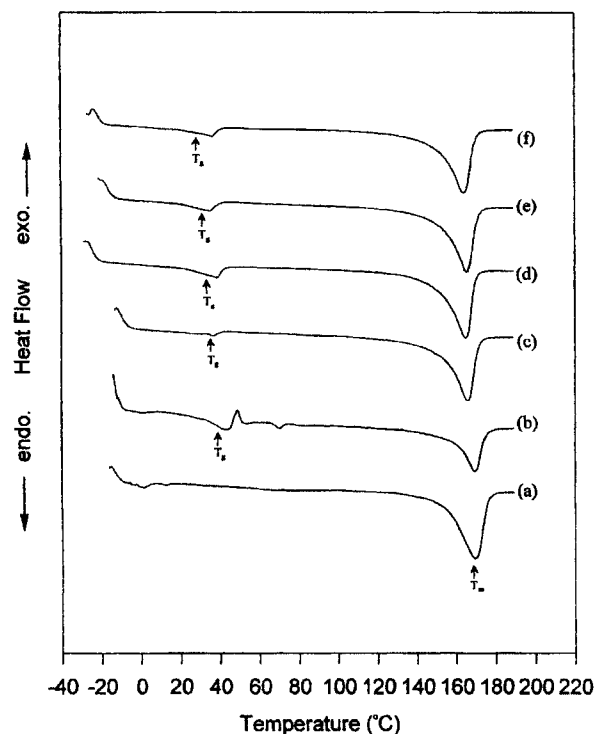


Figure 7 DSC diagram of (a) PP and the FRPP with (b) PVAc and products (c) S04, (d) S05, (e) S06, and (f) S07.

and 8(c) with the same microscope rate, we do not find in Figure 8(c) the obvious-sized dispersed phase in Figure 8(a). No similar dispersed phase was found even in the higher rate of Figures 8(d) and 8(e). The other difference is the change of phase morphology. The phase morphology was changed from a continuous phase and a dispersed phase to two continuous phases. These changes caused by flame-retardant S polymers were caused by the stearyl group, which offers a good matrix compatibility to the flame-retardant polymers and an interaction force between them and the PP matrix.

CONCLUSIONS

Developing an intumescent FRPP is not an easy task because PP does not produce char under fire. Hence, quite a large amount of a char-promoting agent is usually necessary if an inorganic intumescent flame retardant is employed. The polymer-type intumescent flame retardants designed in this study can play the roles of both dehydrating agent and char-promoting agent; moreover, they provide advantages for the mechanical properties of the FRPP. Their positive effects on the

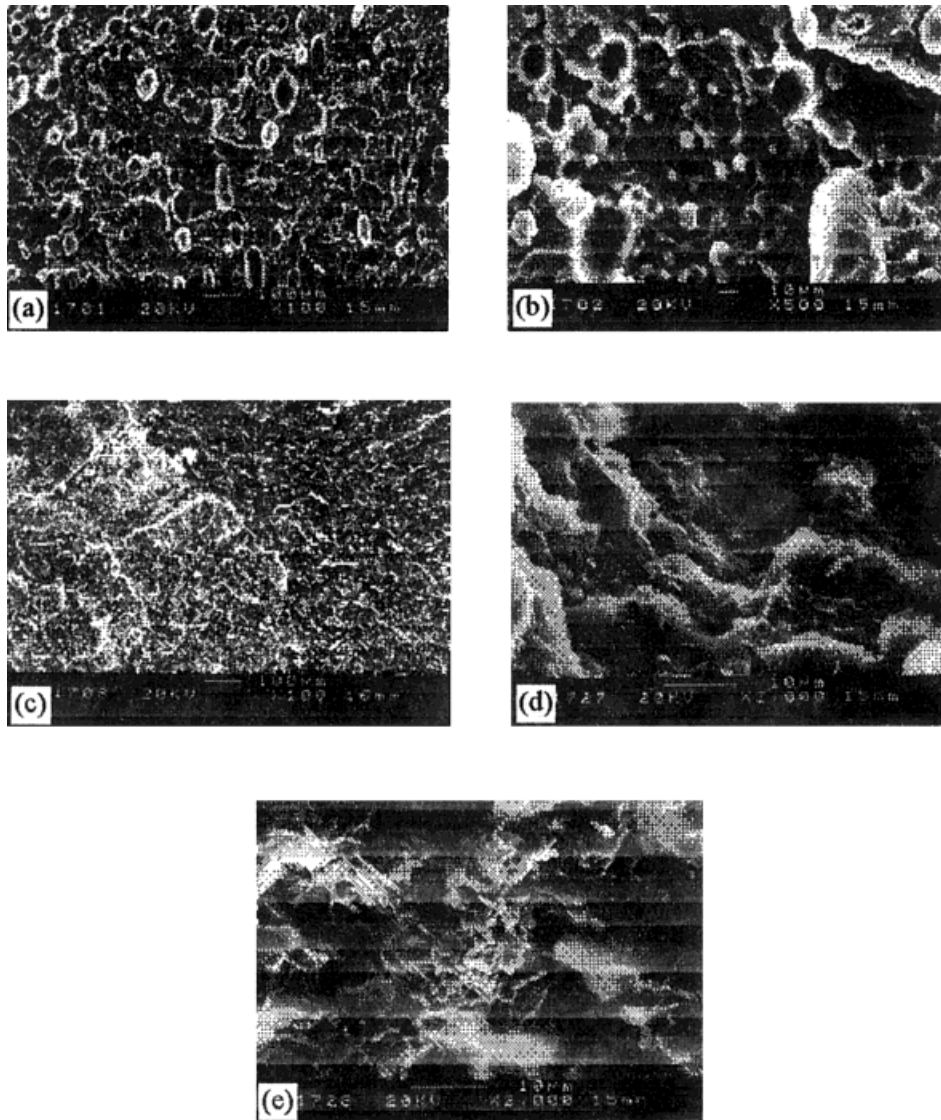


Figure 8 Scanning electron microscope photos of the fracture surface of the FRPP with (a,b) PVAc and products (c) S05, (d) S06, and (e) S07.

impact strength and elongation are not provided by the inorganic additives. Although their effects on the tensile strength and modulus are not so good, it is usually easier to improve the tensile strength and modulus of flame-retardant materials than the impact strength and elongation.

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